

be seen to be drawn, or rather pushed, out in a long conical point, moving much more rapidly than the bubble, and eventually overtaking it and turning over; the fluid at the sides will be still quite uncoloured until mixed by diffusion; to a certain extent the effect is reversible, and the cone of coloured alcohol can be drawn back without mixing very much.

The device shown for preventing evaporation should be in duplicate, one to each limb; only one is shown, as an example.

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*On the Hygroscopic Action of Cotton.*

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In an earlier paper by one of us\* an account was given of the behaviour of dry cotton-wool when immersed in air saturated with water vapour, and the relation between the hygroscopic absorption and the change of temperature which the cotton manifests was investigated. It was shown that, so long as the surrounding air is saturated, the absorption process appears to be unending, though its velocity continuously diminishes; or, in other words, true equilibrium between such an atmosphere and cotton wool, however moist, appears to be impossible, just as it would be impossible between the same atmosphere and an aqueous solution, however dilute. It was pointed out, however, that "if placed in an atmosphere containing water vapour at anything less than saturation pressure (*e.g.*, in the open air) the cotton would in time reach a state of equilibrium, either by absorption or by evaporation, according to its initial condition." As we could find no record of any complete investigation of such relationship, it seemed desirable to determine the amounts of vapour absorbed by a given quantity of cotton in atmospheres of various known degrees of humidity. This has been done; but it has been found necessary to determine the true equilibrium values by approaching them from both sides, by absorption and by evaporation, since neither process becomes really complete in any practicable time, though each leads in a few hours to what might be mistaken for true equilibrium.

Reference must here be made to the interesting work published by Clayton Beadle, in 1894 and 1895,† which was unfortunately entirely

\* 'Roy. Soc. Proc.,' vol. 74, pp. 230—254.

† 'Nature,' vol. 49, p. 457; 'Chem. News,' vol. 71, p. 1; *ibid.*, vol. 73, p. 180.

overlooked by Masson until his attention was called to it after publication of the paper already referred to. Beadle seems to have been the first to observe the striking elevation of temperature that dry cotton undergoes when exposed to damp air and to study the progress of absorption and the course of the temperature change. He, however, did not use atmospheres of constant and known humidity and temperature, but used the open air of the laboratory, so that his curves are affected by considerable irregularities. Apart from these, his results are in general character similar to those we have since obtained.

The experimental method employed by us in this investigation was similar to that already described by one of us.\* The cotton-wool employed was the purified material sold as "absorbent" and was washed several times with boiling distilled water before being used. A suitable quantity, after drying, was wound round the bulb of a thermometer, which was provided with a rubber stopper that closed a jacket-tube in which it could be weighed. By means of this stopper the thermometer could also be inserted into a tube in the cover of a desiccator containing phosphorus pentoxide. It was proved that 24 hours' exposure in this desiccator sufficed to bring the cotton to a constant weight, and this method of drying was adopted throughout in preference to the heating method previously used, as it was suspected that frequent heating to above  $100^{\circ}$  might cause some alteration in the condition of the cotton. The atmosphere of known humidity was obtained in the following way. A glass jar of about 1500 c.c. capacity was provided with a plate-glass cover, ground and lubricated to fit accurately, and a short wide tube was cemented vertically through a central opening in the cover. A cylindrical porous pot of nearly 500 c.c. capacity (cleaned by many previous extractions with acid) was fixed by rubber wedges inside the jar so as to leave a clear space around and below it. The glass jar and porous pot were filled with sulphuric acid solution of known strength, covered, and placed in a thermostat of such depth that only the top of the tube in the cover showed above the water level. The jar was weighted with lead so as to keep it steady when submerged, and the water of the thermostat had free circulation all round and underneath it. Before an experiment the porous pot was emptied by a siphon operating through the central tube, which then served for the admission of the cotton-covered thermometer and also a duplicate instrument without cotton, which was always treated simultaneously and served as a counterpoise in weighing. These were suspended from fixed hooks and could be read accurately to at least a twentieth of a degree by means of a telescope with a micrometer scale.

\* *Loc. cit.*

The interior of the porous pot was kept constant as to humidity by evaporation from its walls, through which filtration of acid occurred, but this infiltration was slow enough to allow of the thermometer hanging for more than 24 hours without risk of the liquid reaching the cotton-wool. The exact strength of the sulphuric acid in each experiment was determined by taking the density of the sample pipetted from the pot, the percentage strength being then read from a curve drawn from Pickering's values for the same temperature.\* This being known, the corresponding vapour pressure was read from a curve drawn with percentage of  $\text{H}_2\text{SO}_4$  as abscissæ and relative vapour pressure (that of water at the same temperature taken as unity) as ordinates. Regnault's values† were used in constructing this curve, and they were supplemented by the very concordant values obtained by a different method by Helmholtz.‡ Such a curve, drawn for  $20^\circ \text{C.}$ , is practically correct also for all neighbouring temperatures, as the relative vapour pressure of a given acid solution is almost constant.

Two sets of apparatus were kept in alternate use so that each porous pot could soak for several days in a new acid solution before tests were made with it. A third apparatus was reserved for distilled water so as to provide a saturated atmosphere when required.

The sulphuric acid employed for making up the solutions was subjected to a preliminary treatment for complete removal of oxides of nitrogen. Unless this is done, the cotton is to some extent affected by exposure over the higher strengths of acid; it tends to become brittle and its hygroscopic power is sensibly diminished.

For convenience, our results are discussed in the sequel under six heads.

1. *The Determination of the Conditions for Equilibrium.*—In order to ascertain the weight of absorbed moisture which puts a given weight of cotton into true equilibrium with an atmosphere of given humidity, it is not sufficient to expose the dry cotton to the action of that atmosphere till its weight becomes apparently constant, for the rate of absorption, which rapidly diminishes, becomes almost inappreciable, while the absorption itself is certainly incomplete. This is proved by supersaturating the cotton by previous exposure over water or a more dilute acid and then again immersing it in the original atmosphere. It now loses moisture by evaporation till it once more attains an apparently constant weight; but this is considerably greater than that previously reached by absorption. The thermometer on which the cotton is wound serves the useful purpose of indicating the

\* 'Chem. Soc. Trans.,' vol. 57, pp. 152—156.

† Quoted in 'Carnelley's Tables,' vol. 11, p. 750.

‡ 'Wied. Ann.,' vol. 27, p. 508.

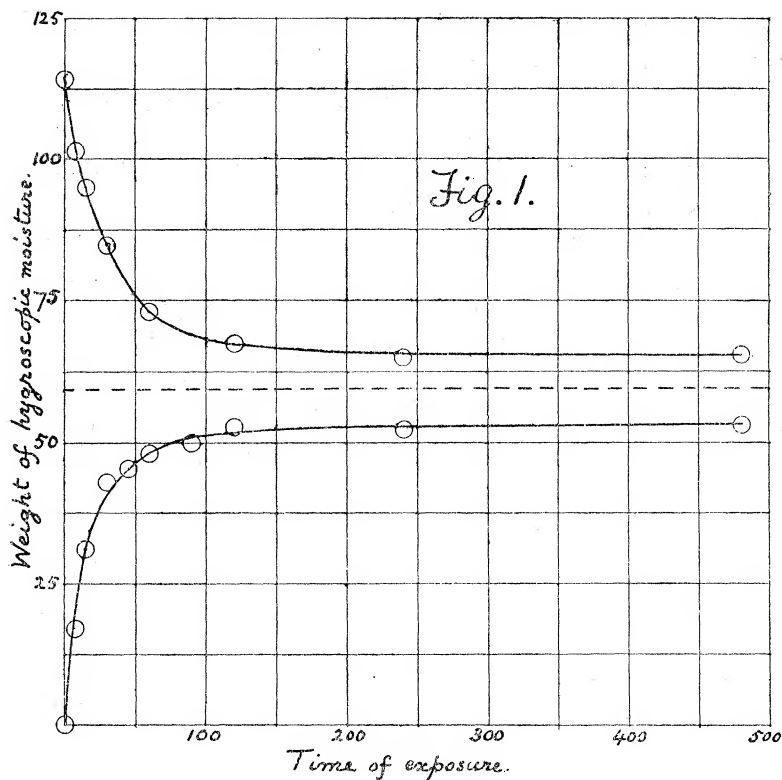
progress of either change; for during the absorption test it rises rapidly for a few minutes and then falls with diminishing velocity towards the temperature of the thermostat (as previously described),\* and this process is reversed during the evaporation test when the thermometer falls quickly to a minimum and then rises with diminishing velocity towards the temperature of the environment. In order to render these indications accurate, it is necessary to suspend the thermometer protected by its jacket-tube in the apparatus for an hour or two before the test is begun, so that it may have the same temperature as the thermostat at the moment of exposure. The figures given in Table I and the corresponding curves (fig. 1) illustrate the characteristic behaviour of dry cotton and of supersaturated cotton. The acid used in these tests contained 40·5 per cent. of  $\text{H}_2\text{SO}_4$ , corresponding to a relative vapour pressure of 0·556. The acid strength was proved to remain constant throughout the series. Each point in the absorption and evaporation curves was obtained by an independent experiment. The excess moisture required for each evaporation test was imparted by exposure over water, the time necessary for imparting a definite quantity of moisture being read off from a curve drawn from previous experiments to show the course of absorption in a saturated atmosphere. It is possible in this way to predetermine the imparted moisture accurately to within

Table I.—0·948 gramme of cotton exposed over acid of 40·5 per cent.  $\text{H}_2\text{SO}_4$ .  
 $p/P = 0\cdot556$ . Bath at  $20^\circ \text{C}$ .

Absorption tests.		Evaporation tests.	
Time of exposure (minutes).	Moisture absorbed (gramme).	Time of exposure (minutes).	Moisture retained (gramme).
0	0	0	0·1140
7·5	0·0170	7·5	0·1015
15	0·0312	15	0·0950
30	0·0430	30	0·0847
45	0·0453		
60	0·0480	60	0·0730
90	0·0500		
120	{ 0·0526 }	120	0·0674
	{ 0·0530 }		
240	0·0522	240	{ 0·0648 }
			{ 0·0654 }
480	0·0530	480	0·0655

Mean value of absorption and evaporation results ..... { 0·0601 at 120 minutes.  
 0·0586 „ 240 „  
 0·0592 „ 480 „

\* *Loc. cit.*



about a milligramme. The quantity here used was rather less than double that indicated for true equilibrium, viz., 114 instead of 118 milligrammes.

As is seen from the results, this true equilibrium value must lie somewhere between the apparent limits of absorption and evaporation, and their arithmetic mean may be taken as sufficiently correct.

The time allowed for absorption or evaporation in any particular case has depended on the strength of the acid, and has varied from four hours in the driest to 24 in the most humid atmospheres employed, experience showing that longer exposure within practicable limits would not appreciably affect the results. As a rule, the initial moisture imparted before an evaporation test was about double that required for equilibrium; but any deviation from this rule produces no sensible difference in the final result, as it merely hastens or retards the initial evaporation and is thus in a measure self-compensating.

To avoid circumlocution, the following symbols are used in the sequel:—

W is the weight of dry cotton employed.

T is the temperature of the apparatus.

$p$  is the actual pressure of water-vapour in the atmosphere employed.

$P$  is the saturation pressure of water-vapour at the same temperature.

$M_A$  is the weight of moisture absorbed by the sample of dry cotton of weight  $W$  after exposure in the apparatus till further absorption appears negligible.

$M_E$  is the weight of moisture retained by the same sample after it has been supersaturated by exposure over water and then allowed to evaporate in the apparatus till further loss appears negligible.

$M$  is the arithmetic mean of  $M_A$  and  $M_E$ , and is taken as indicating the amount of absorbed moisture which is required to establish true equilibrium.

2. *The Influence of Temperature.*—The  $M$  values obtained with a given sample of cotton depend on the strength of sulphuric acid over which it is exposed, but not upon the temperature. In other words, they depend upon the relative vapour pressure (the saturation pressure of water-vapour being taken as unity), and not on the absolute vapour pressure of the enveloping atmosphere, for the relative vapour tension of any given sulphuric acid solution is practically independent of the temperature. It seems, therefore, that cotton containing a definite proportion of moisture resembles an aqueous solution in that it also follows Babo's law, *i.e.*, exercises a vapour tension which is at different temperatures a constant fraction of that of pure water.

The following tests (Table II) illustrate this. They were all made with the same sample of cotton. It was subsequently shown to have been somewhat altered by previous exposure over impure sulphuric acid, and was

Table II.

(1) Acid of density 1.4245 at 25°; 53.5 per cent.  $H_2SO_4$ ;  $p/P = 0.30$ .

T.	$p$ .	$M_A$ .	$M_E$ .	$M$ .
20°	5.2	27.5	28.9	28.2
25°	7.1	27.8	29.6	28.7
30°	9.5	26.5	28.0	27.2

(2) Acid of density 1.3340 at 25°; 44.0 per cent.  $H_2SO_4$ ;  $p/P = 0.49$ .

T.	$p$ .	$M_A$ .	$M_E$ .	$M$ .
20°	8.5	40.5	42.4	41.4
25°	11.5	39.0	43.5	41.2
30°	15.5	39.5	41.5	40.5

(3) Acid of density 1.2818 at 25°; 38.0 per cent.  $\text{H}_2\text{SO}_4$ ;  $p/P = 0.615$ .

T.	$p$ .	$M_A$ .	$M_E$ .	M.
20°	10.7	47.7	52.3	50.0
25°	14.5	47.9	51.1	49.5
30°	19.4	47.8	51.7	49.8

therefore, not used in further work, but this does not affect the conclusions drawn here. The values of  $M$  are given in milligrammes and those of  $p$  in millimetres of mercury.

3. *If different quantities of the same quality of cotton* be employed, the weight of moisture required to establish equilibrium with an atmosphere of given humidity is in constant ratio to the weight of the cotton. In the following tests not only the weights of cotton-wool were varied, but also the mode of wrapping it, some samples being wound tightly and others more loosely round the supporting thermometer. This makes no sensible difference in the final  $M$  value, though, of course, it may to some extent influence the velocity of absorption or evaporation by affecting the freedom of access of the moist air to the surface of the fibres.

Table III.—Acid of density 1.1398 at 20° C.; 20.3 per cent. of  $\text{H}_2\text{SO}_4$ ;  
 $p/P = 0.874$ ; weights in grammes.

W.	$M_A/W$ .	$M_E/W$ .	$M/W$ .
1.0228	0.1105	0.1329	0.1217
0.9480	0.1102	0.1319	0.1210
0.6227	0.1132	0.1361	0.1247
0.5165	0.1084	0.1332	0.1208
0.4680	0.1053	0.1357	0.1205

These results, taken in conjunction with those given in the last section, suffice to show that, for a given quality of cotton wool, the value of  $M/W$  depends only on that of  $p/P$ .

4. *The Influence of Surface.*—It is obvious that the weights of different samples of the same cotton wool, having the same average dimensions of fibre, are proportional to the extents of surface exposed to the hygroscopic action, and so that the constancy of the ratio  $M/W$  in their case gives no proof that  $M$  is really a function of the mass of cellulose rather than of its surface. It may, of course, be both. To test this question properly it is desirable to employ cellulose preparations having various known ratios of surface to mass. This is, however, not very easily done. The individual

fibres in any given bundle of cotton vary considerably, and only a very laborious microscopic examination could give a reliable estimate of the average dimensions. Moreover, for a fair comparison, all the samples would require similar previous treatment in order to obviate not only errors due to residual impurity, but also such unequal alterations of the cellulose molecule itself as are at least possible in the case of so complex a substance. For this reason, experiments with amorphous cellulose, obtained by one of the solution methods, might give results not fairly comparable with those from cotton fibre, even if all ordinary impurities were eliminated. Such experiments, if carried out with all precautions, might, however, afford information of value and help to settle the question of whether the surface film of moisture does, as suggested by one of us,\* diffuse osmotically into the substance of the cellulose and form with it a solid solution. A few tests already made with pure filter paper may be cited. The paper used was Schleicher and Schüll's ash-free, No. 589. Three papers of 7 cm. diameter were wrapped tightly round the bulb of a thermometer and secured with a few turns of cotton thread, and then well washed and dried before use. The dry weight of paper (and thread) was 0.918 gramme. The *M* values were determined over three different strengths of acid, and may be compared with the corresponding values for cotton wool, which have been read from the curve shown in fig. 2. It will be seen that they are somewhat higher, weight for weight, in the case of the filter paper, but that the difference is not great.

Table IV.—Tests with Filter Paper.

W = 0.918 gramme; bath at 20° C.

Acid employed.			M <sub>A</sub> .	M <sub>E</sub> .	M.	Filter paper. M/W.	Cotton wool. M/W.
<i>d</i> <sub>20°</sub> .	H <sub>2</sub> SO <sub>4</sub> p. c.	<i>p</i> /P.					
1.3866	49.3	0.360	0.0410	0.0482	0.0446	0.0486	0.0456
1.2899	38.9	0.596	0.0582	0.0724	0.0653	0.0711	0.0676
1.1986	27.6	0.768	0.0827	0.0971	0.0899	0.0980	0.0920

5. *The relation between the moisture content and the vapour tension* of any given preparation of pure cotton may be shown by a curve, plotting *M*/*W* as abscissæ and *p*/*P* as ordinates. The experimental method employed is applicable over a large range, but becomes unworkable when *p*/*P* exceeds about 0.97, since there is in practice a limit to the time that can be given

\* *Loc. cit.*



for absorption or evaporation over acid or for supersaturation over water as a preliminary to the evaporation test. It is, however, obvious that the method must in any case be inapplicable to that value of  $M$  (if there be one) which corresponds to the full saturation pressure, for exposure over water for any length of time would, at the best, give only  $M_A$ , which is less than  $M$ , and it would be impossible to supersaturate the cotton and then determine the  $M_E$  value by evaporation over water. These considerations support our previous contention that no true equilibrium is possible between cotton, however moist, and saturated aqueous vapour. In other words, the approach of the curve in fig. 2 to the saturation pressure is probably asymptotic. In this connection it is instructive to contrast the time-absorption curve in an unsaturated atmosphere (fig. 1) with that showing a 12-hours' absorption over water.\*

The first series of experiments made for the purpose of testing the variation of  $M/W$  with  $p/P$  was spoilt by the use of insufficiently purified sulphuric acid, for it was found that the cotton had become brittle and so altered in the course of the work that points re-determined did not fall on the curve. A better result was obtained in the series given below. Here 15 different strengths of specially purified acid were used in the order indicated in the table, and the fact that the first two points determined lie practically on the curve formed by joining the later ones is sufficient guarantee that no appreciable change in the hygroscopic power of the cotton

Table V.—Hygroscopic Tests with 0.948 gramme of Pure Cotton over Sulphuric Acid Solutions (at 20° C.).

Order of test.	Acid employed.			$M_A$ .	$M_E$ .	$M$ .	$M/W$ .
	$d_{20^\circ}$ .	$H_2SO_4$ p. c.	$p/P$				
3	1.6516	73.8	0.050	0.0120	0.0145	0.0132	0.0139
4	1.5724	67.0	0.100	0.0175	0.0198	0.0186	0.0196
5	1.4850	59.0	0.198	0.0264	0.0311	0.0288	0.0304
6	1.4167	52.6	0.294	0.0356	0.0406	0.0381	0.0402
7	1.3672	47.2	0.408	0.0441	0.0497	0.0469	0.0495
8	1.3282	43.1	0.500	0.0509	0.0593	0.0551	0.0581
2	1.3028	40.5	0.556	0.0530	0.0655	0.0592	0.0624
9	1.2887	38.8	0.598	0.0599	0.0690	0.0644	0.0679
10	1.2368	32.3	0.710	0.0716	0.0840	0.0778	0.0821
11	1.1930	26.8	0.794	0.0860	0.1002	0.0931	0.0982
13	1.1616	23.2	0.844	0.0989	0.1107	0.1048	0.1106
1	1.1398	20.3	0.874	0.1045	0.1250	0.1148	0.1210
12	1.1226	18.1	0.894	0.1114	0.1300	0.1207	0.1274
14	1.0686	10.3	0.952	0.1378	0.1606	0.1492	0.1574
15	1.0378	6.2	0.972	0.1563	0.1792	0.1678	0.1770

\* See 'Roy. Soc. Proc.,' vol. 74, p. 244.

occurred in the course of the work. The general form of the curve was quite similar in the first series, though the exact values were not trustworthy. It is obvious that such a curve indicates the relative water-vapour tensions of cotton of different degrees of moistness.

The numbers in the fourth and eighth columns of this table have been used in plotting the curve shown in fig. 2.

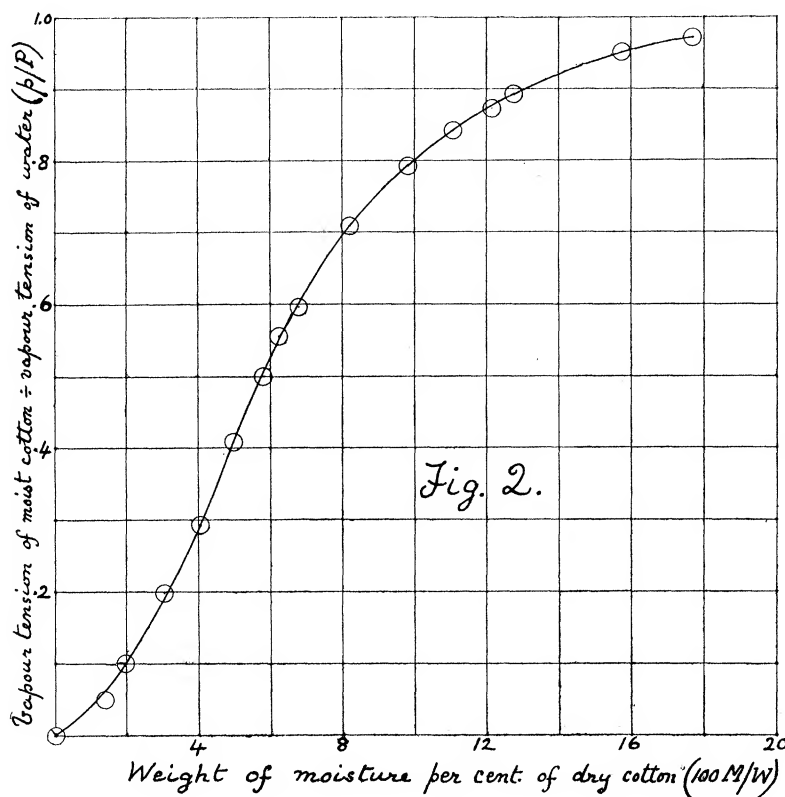


Fig. 2.

6. *A New Method of Hygrometry.*—The initial velocity with which any given sample of dry cotton wool absorbs moisture at the moment of its exposure must depend on the pressure of water-vapour in the atmosphere to which it is exposed and on conditions of surface, etc., which are constant for that particular sample. Now it has already been shown by one of us that the heat production is always proportional to the amount of hygroscopic absorption; and as, at the first moment of exposure, when the cotton is dry and at the same temperature as its environment, the heat produced may be regarded as entirely consumed in raising the temperature of the cotton, it follows that the initial rate of that rise is directly proportional to the

pressure of aqueous vapour. Adopting the same notation as in the previous paper, viz:—

$t$  = time since exposure of the dry cotton,

$\theta$  = difference of temperature between the cotton and its environment,

$m$  = weight of moisture absorbed,

$p$  = pressure of water-vapour in the atmosphere surrounding the cotton,

we may express the above conclusions briefly thus:—

$$\left(\frac{d\theta}{dt}\right)_0 \propto \left(\frac{dm}{dt}\right)_0 \propto p.$$

Now it was shown\* that the whole temperature curve, in the case of immersion of dry cotton in saturated vapour, is expressed with very fair accuracy by the equation

$$\theta \left(t + \frac{\tau^2}{t}\right) = 2\tau\phi,$$

where  $\phi$  is the maximum value attained by  $\theta$ , and  $\tau$  is the corresponding value of  $t$ . Later results confirm this, and it follows that at any moment ( $t$ )

$$\frac{d\theta}{dt} = 2\tau\phi \frac{\tau^2 - t^2}{(\tau^2 + t^2)^2};$$

and therefore that

$$\left(\frac{d\theta}{dt}\right)_0 = 2 \frac{\phi}{\tau}.$$

If this equation holds also for cases of immersion in unsaturated water-vapour, we arrive at the conclusion that  $\phi/\tau$  should be proportional to  $p$ , or that  $\phi/\tau = kp$ , where  $k$  is a constant for the particular sample of cotton, or rather for the instrument, which consists of the thermometer and its cotton covering

This conclusion is fairly justified by the following observations. The first set was designed to test the constancy of  $k$  when the air in the apparatus was saturated with water-vapour at different temperatures. The results are shown in the following table for temperatures between 15° and 35° C. Above 35°,  $k$  appeared to diminish; but considerable error is probably caused when there is a large difference between the temperature of the thermostat and that of the outer air, especially as a short exposure of the thermometer to the latter is unavoidable when it is being withdrawn from its jacket-tube before immersion.

The next series of tests was made with a different thermometer and covering of cotton wool. Eleven tests in air saturated with water-vapour at 20° gave for this instrument a mean  $k$  value of 0.140, the extremes being

\* *Loc. cit.*

Table VI.—Dry Cotton-covered Thermometer ("F") exposed over Water at various Temperatures.

T.	$p$ (mm. of mercury).	$\phi$ (degrees C.).	$\tau$ (minutes).	$\phi/\tau$ .	$\phi/p\tau = k$ .
15°	12·7	9·6	6·5	1·48	0·116
"	"	9·7	6·85	1·41	0·112
"	"	9·6	6·8	1·41	0·111
20°	17·4	11·25	5·65	1·99	0·114
"	"	11·55	5·6	2·06	0·119
25°	23·5	12·95	4·85	2·67	0·114
"	"	13·1	4·9	2·67	0·114
30°	31·5	14·25	4·05	3·52	0·112
"	"	14·0	4·1	3·41	0·109
35°	41·8	15·4	3·55	4·34	0·104
"	"	15·7	3·45	4·55	0·109

Mean value of  $k = 0·112$ .

0·136 and 0·145. The same instrument was used for the determination of the  $M$  values already quoted in Table V, and simultaneous determinations of the  $\phi$  and  $\tau$  values were made during the exposures over the sulphuric acid solutions used for that purpose. In the case of the three strongest acids, giving atmospheres less than one-fifth saturated, the errors due to the unavoidable exposure of the instrument to the outer air at the start and to other causes bulk too largely for any reliance to be placed on the results, but in 11 tests with more dilute acids  $k$  is seen to have a mean value of 0·137, with extreme values of 0·127 and 0·146, and is thus not far from constant and equal to its value in saturated air. These results are shown in the following table:—

Table VII.—Dry Cotton-covered Thermometer ("G") exposed over Water and Sulphuric Acid Solutions at 20° C.

$p/P$ .	$p$ (mm. of mercury).	$\phi$ (degrees C.).	$\tau$ (minutes).	$\phi/\tau$ .	$\phi/p\tau = k$ .
0·294	5·1	4·40	6·38	0·69	0·135
0·408	7·1	5·73	6·35	0·90	0·127
0·500	8·7	6·96	6·07	1·15	0·132
0·556	9·7	7·42	5·86	1·27	0·130
0·598	10·4	7·98	5·97	1·34	0·128
0·710	12·4	9·56	5·55	1·72	0·139
0·794	13·8	10·36	5·47	1·89	0·137
0·844	14·7	10·94	5·24	2·09	0·142
0·894	15·5	11·54	5·16	2·24	0·144
0·952	16·6	12·40	5·10	2·43	0·146
0·972	16·9	12·44	5·12	2·43	0·144
1·000	17·4	12·47	5·11	2·44	0·140

The figures in the last horizontal line are the means of those obtained from 11 determinations by exposure over water.

A third series of tests was made with the same instrument ("G") in order to ascertain whether the value of  $k$  is different when the dry cotton is exposed in the open air from that already found by exposing it over water or sulphuric acid solutions in the experimental apparatus. For this purpose observations were made on 10 consecutive days (December, 1905) by exposing "G" to the air of the laboratory and taking simultaneous readings of wet and dry bulb thermometers, which were interpreted by Apjohn's formula so as to give the pressure of aqueous vapour. All readings were made by telescope so as to avoid errors which arise from proximity of the observer, and the necessary corrections were applied after comparison of the thermometers with a standard one. The results are shown in the following table:—

Table VIII.—Dry Cotton-covered Thermometer ("G") exposed to the Air of the Laboratory with Simultaneous Wet and Dry Bulb Hygrometry.

Dry bulb.	Wet bulb.	Bar.	$p$ (mm. of mercury).	$\phi$ (degrees C.).	$\tau$ (minutes).	$\phi/\tau$ .	$\phi/p\tau = k$ .
17°23	13°46	750	9·54	7·43	5·53	1·344	0·141
16°30	12°70	757	9·06	6·80	5·54	1·227	0·135
16°28	13°33	762	9·85	7·50	5·58	1·345	0·136
17°70	14°48	762	10·58	7·86	5·53	1·421	0·134
18°39	15°28	761	11·29	8·26	5·26	1·570	0·139
17°66	14°70	759	10·90	8·06	5·25	1·536	0·141
18°50	14°72	759	10·47	7·56	5·40	1·400	0·134
20°84	16°85	759	12·19	8·19	4·87	1·682	0·138
23°80	18°32	756	12·81	7·61	4·53	1·680	0·131
19°88	15°48	761	10·75	7·30	5·14	1·420	0·132

From these tests it is seen that  $k$  varies between 0·131 and 0·141, with a mean value of 0·136, which agrees well with the mean values obtained by exposure over water (0·140) and over varying strengths of sulphuric acid (0·137) in the porous pot of the experimental apparatus.

It follows that such an instrument supplies us with a method of hygrometry which is fairly accurate and easy to use. The method may be worked in the following manner. A suitable thermometer is passed through the bore of a rubber cork, which is fixed in a convenient position on the stem. About a gramme of cotton wool is then wound round the bulb and secured by a few turns of cotton thread. Filter paper may be used instead of cotton wool, and is perhaps more convenient, being less bulky. A desiccator is conveniently constructed by placing a quantity of phosphorus

pentoxide at the bottom of a large wide-mouthed bottle, closed by a rubber stopper through which passes a short glass tube wide enough to admit the thermometer and be closed by its rubber cork. With this arrangement there is no risk of the cotton wool coming into contact with pentoxide. The instrument is always kept in the desiccator except when in actual use, and if observations are taken once in 24 hours the interval is sufficient to ensure dryness. When an observation is to be made, the thermometer is read through a telescope. It is then removed from the desiccator and hung near it, a stop-watch being started at the moment of exposure. The rise of temperature is noted and, as this slows down, a few readings of time and temperature are made at short intervals; and these are repeated as the same temperatures are passed during cooling from the maximum. Two or three points in the neighbourhood of this maximum are sufficient. The thermometer is then replaced in the desiccator, which is left in position for the next observation. The difference between the initial and maximum temperatures gives  $\phi$ . The corresponding time ( $\tau$ ), which cannot be directly observed with sufficient accuracy, is calculated by the rule involved in the equation for the curve, already discussed, that  $\tau = (t_1 t_2)^{\frac{1}{2}}$ , where  $t_1$  and  $t_2$  are the two observed times at which the same temperature (near to  $\phi$ ) is passed. The following example will illustrate the method:—

Temperature.	$t_1$	$t_2$	$(t_1 t_2)^{\frac{1}{2}}$ .
18°06	0	0	—
25°28	3' 0"	9' 7"	5°23 mins.
25°56	3 23	8 12	5°27 "
25°84	3 53	7 6	5°25 "
26°12 (max.).	—	—	—

Hence

$$\phi = 26.12 - 18.06 = 8.06,$$

and

$$\tau = 5.25 \text{ (mean value).}$$

In order to find the pressure of aqueous vapour in the atmosphere from such observations, the value of  $k$  in the equation  $p = \phi/k\tau$  must be once for all determined for the particular instrument employed, and this may be done with sufficient accuracy by taking the average result of a few exposures in atmospheres with known values of  $p$ ,—say over water at known temperatures.

It is not claimed that this method of hygrometry is to be preferred to the usual wet and dry bulb method for ordinary purposes, but it may prove useful in special cases.

*Summary of Results.*

1. The quantity of hygroscopic moisture required by a given quantity of cotton to put it in true equilibrium with an atmosphere of given humidity, below the saturation value, can be ascertained by taking the mean of the apparent equilibrium values reached by absorption (cotton initially dry) and evaporation (initially over-moist). The progress of either change can be followed by observing the characteristic temperature curve given by a thermometer the bulb of which is covered by the cotton.

2. The vapour tension of any sample of cotton containing a definite quantity of moisture is at different temperatures (at least within ordinary atmospheric range) the same fraction of that of water. The law here is similar to that familiar (Babo's law) in the case of aqueous solutions.

3. Different weights of the same cotton have the same vapour tension when they contain the same percentage weights of hygroscopic moisture. The results are not influenced by tight or loose packing.

4. Filter paper gives results very similar to those obtained with cotton wool; *i.e.*, the same vapour tension corresponds to but slightly different percentage weights of hygroscopic moisture.

5. The vapour-tension curve of moist cotton wool, in which the relative vapour tension (that of water taken as unity) is plotted against percentage weight of hygroscopic moisture, has been determined from  $p = 0$  to  $p = 0.97 P$ . Its approach to  $p = P$  is probably asymptotic.

6. A new method of hygrometry has been tested, and is described, which is based upon the observations of the rate of rise of temperature of dry cotton when first exposed to moist air.

*Postscript.*—Since the foregoing paper was written, we have received the last number of the 'Proceedings of the Royal Society' (No. A 517) containing a paper by Professor Trouton and Miss Pool on "The Vapour Pressure in Equilibrium with Substances holding Varying Amounts of Moisture," which was read at the Society on January 25. As the questions dealt with in the two papers are essentially the same, though the methods employed are different, we may be allowed to state that our experimental work (except the few tests with filter paper recorded in Table IV) was done during 1905 in Melbourne, and in ignorance of the fact that Professor Trouton was similarly engaged.

Trouton's method differs from ours in that he seeks to ascertain the vapour pressure corresponding to a predetermined quantity of moisture, while we have sought to ascertain the amount of hygroscopic moisture which balances

a predetermined vapour pressure. Trouton and Pool have used flannel, which is not a pure material, but in a footnote state that cotton wool has given similar results. Perhaps the most striking of their results is the establishment of the law which has been discussed in the second section of this paper, viz.:—that the ratio of the vapour tension of a hygroscopically moist substance to that of water is independent of the temperature, and of this they give much fuller evidence than we have adduced. In another respect the results obtained by the two methods are in agreement, viz., as to the form of the lower part of the curve for vapour tension and weight of moisture, where a characteristic change of curvature is exhibited. Trouton, however, finds that a parabolic formula fits the upper portion of his curve, pointing to the attainment of the full vapour tension of water itself by material containing only a limited amount of moisture, while our values cannot be so expressed and we incline to doubt the possibility of any such true equilibrium with saturated water-vapour.

No exact quantitative comparison is possible between Trouton and Pool's values and ours because, though they give the weight of the flannel in grammes, they state the quantities of added water in terms of an arbitrary unit, viz., the contents of a capillary tube the dimensions of which are not given. This is all the more disappointing that their paper opens with the statement that "the knowledge of the quantity of water held under varying circumstances by substances of an absorbent character, such as cotton or woollen material, in an atmosphere of any given humidity, is not only of importance in hygrometry, but is also of general interest in connection with the processes used in drying such materials. No investigations, however, of this subject seem, up to the present, to have been ever published." Surely such investigations, when made, lose much of their value when the results are given in terms of units that cannot be interconnected. Perusal of the paper, however, suggests the probable explanation, viz., that Trouton believes that the whole hygroscopic moisture is permanently retained as a surface film, in which case it would be useless to give its actual weight without a correct measure of the exposed surface, which can hardly be obtained. We gather this impression of Trouton's views despite the fact that he himself calls attention, as we have done, to the similarity of the moist material to an aqueous solution in respect to the influence of temperature on vapour tension, and that he specially points out the general similarity between the isothermals for water in flannel and for water in sulphuric acid. The fact should be emphasised, however, that anything more than a very rough agreement between these is not to be expected, even if the moist flannel be regarded as a species of aqueous solution, for the sulphuric acid case is, of



course, greatly complicated by ionisation, the effects of which are for the most part entirely unknown, but are certainly quite different in different parts of the curve. Aqueous solutions of such a substance as glycerine would be much more instructive for comparison, but, so far as we know, there are no data for a complete curve in that or any similar case.

In our opinion the pure surface theory which seems to be held by Trouton is inconsistent with known facts and accepted views concerning the behaviour and functions of cellulose and similar substances; and, unless special evidence be adduced to prove that they are actually impermeable by water, it is only reasonable to assume that the surface film of moisture does (until equilibrium is reached) penetrate and form a species of solution. We hope to offer further evidence on this point later.

In the meantime, the following comparison of Trouton's results for flannel (second series) and ours for cotton shows the extent to which they agree with or differ from one another. The values for the moisture corresponding to the same stated values of  $p/P$  have in both cases been read from the curves and, as already explained, are in units that cannot be compared; but it will be seen that the ratios in the last column of the table are fairly constant for middle values of pressure, but diverge at both ends. It seems to us that this divergence at the higher pressures is probably attributable to want of true equilibrium in Trouton's experiments, for our own experience has shown that the attainment of such equilibrium within 12 hours—or even a much longer period—of the admission of water to hygroscopic material is not possible. This error would not interfere with the demonstration of the temperature law given by Trouton and Pool, for we could have based our proof of it on either the absorption or the evaporation tests as well as on the

$p/B.$	Moisture in flannel in arbitrary units (Trouton).	Moisture in cotton, in percentage (M. and R.).	<u>Trouton's value.</u> <u>M. and R.'s value.</u>
0·05	1·6	1·16	1·38
0·1	2·8	1·92	1·46
0·2	4·8	3·14	1·53
0·3	6·4	4·14	1·55
0·4	8·0	4·92	1·63
0·5	9·6	5·76	1·67
0·6	11·6	6·80	1·71
0·7	14·0	8·08	1·73
0·8	16·5	9·94	1·66
0·85	18·0	11·3	1·59
0·9	19·6	13·0	1·51
0·95	21·9	15·7	1·40
0·975	23·2	18·0	1·29
1·0	28·0	—	—

mean (true) values; but it would materially affect the other conclusions and especially the statement that the moist material attains to the full vapour tension of pure water when it contains a definite quantity of moisture. Unless very strong and direct evidence were forthcoming, we could not, after our own experience, believe that the whole of each "feed" of water driven over into the space containing the flannel was uniformly distributed as hygroscopic moisture throughout that substance before the vapour pressure was measured, or that no part of the final "feeds" was left as ordinary liquid water to exert its influence.

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*Calcium as an Absorbent of Gases for the Production of High Vacua and Spectroscopic Research.*

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I.—*Introductory.*

This paper contains an account of researches carried out by the aid of an electric furnace designed to heat reagents in soft glass tubes up to temperatures far above the softening point of glass, and has special reference to the use of calcium under these conditions as a valuable absorbent of gases. Recent work on the generation of helium from the radio-elements